Kondo-Cluster-Glass State near a Ferromagnetic Quantum Phase Transition

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We report on a comprehensive study of $CePd_{1-x}Rh_x$ ($0.6 \leq x \leq 0.95$) poly- and single crystals close to the ferromagnetic instability by means of low-temperature ac susceptibility, magnetization and volume thermal expansion. The signature of ferromagnetism in this heavy-fermion system can be traced from 6.6 K in CePd down to 25 mK for $x = 0.87$. Despite pronounced non-Fermi-liquid (NFL) effects in both, specific heat and thermal expansion, the Grüneisen ratio *does not* diverge as $T \rightarrow 0$, providing evidence for the absence of a quantum critical point. Instead, a peculiar "Kondo-cluster-glass" state is found for $x \geq 0.65$, and the NFL effects in the specific heat, ac susceptibility and magnetization are compatible with the quantum Griffiths phase scenario.

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The ground state of f-electron-based Kondo-lattice (KL) systems depends sensitively on the balance between Kondo- and exchange interactions. While recently numerous antiferromagnetic (AF) KL systems have been tuned towards a quantum critical point (QCP) by variation of pressure or doping [1], appropriate KL candidates for the study of ferromagnetic (FM) QCPs are extremely rare [2]. Starting deep in the localized moment regime, in several Ce-based ferromagnets the increase of the Kondo interaction with pressure tends to stabilize an AF ground state before the QCP is reached [3, 4]. Binary CePt may be an exception [5], although the FM signature is dramatically weakened under pressure well before the ordering temperature vanishes, and transport experiments suggest a sudden drop of the phase boundary close to the critical pressure. This behavior resembles the case of pure FM transition-metal compounds, which display first-order quantum phase transitions (QPTs) under pressure [6, 7, 8].

Theoretical studies have suggested that the suppression of itinerant ferromagnetism in clean systems, in contrast to antiferromagnetism, always ends at a classical critical point (at finite T) where a first-order phase transition occurs [9, 10]. For KL systems it is questionable whether all QCPs could be described in an itinerant scenario [11]. Thus, a detailed investigation of suitable FM systems close to their instability is highly desired. Furthermore, theoretical calculations show that disorder in a system may smear out the QPT, resulting in an exponential suppression of the ordered state [12]. In fact, experiments on doped FM materials as, e.g., the itinerant $Zr_{1-x}Nb_xZn_2$ [13] or the $5f$-based heavy-fermion (HF) system $URh_{1-x}Ru_xGe$ [14] exhibited a continuous depression of the ordered state.

In this Letter, we investigate the KL system $CePd_{1-x}Rh_x$, which is an ideal candidate to explore a FM QPT as it provides the opportunity to investigate the evolution of FM ordering by tuning the substitution of the Ce ligands. The system evolves from a FM ground state in CePd with $T_C = 6.6$ K to a non-magnetic intermediate-valence (IV) state in CeRh. The whole series crystallizes in the orthorhombic CrB structure. The observed decrease of T_C over more than two decades in temperature, from 6.6 K at $x = 0$ to 25 mK at $x = 0.87$, is presently the best known example for the continuous disappearance of FM order in any KL system [15, 16].

Evidence for the FM nature of the ordered state stems from the temperature dependence of the ac susceptibility which shows sharp maxima for all investigated samples. The competition between FM order and, with increasing Rh content, growing Kondo screening leads to a continuous decrease of T_C. Furthermore, the smaller Rh gives rise to a volume compression of the compound's unit cell and changes its electronic structure. Most interestingly, the curvature of the phase boundary $T_C(x)$ changes from negative for $x < 0.6$ to positive for $x \geq 0.6$, displaying a long tail towards higher Rh contents. In this concentration range, the Kondo temperature $T_K \approx \Theta_p/2$ (Θ_p: paramagnetic Weiss temperature) strongly increases with x [16].

Specific-heat measurements have proved the existence of NFL behavior for concentrations close to the disappearance of FM order [17]. At $x = 0.85$ a logarithmic increase of the specific-heat coefficient $\gamma = \Delta C(T)/T$ down to the lowest temperature of 80 mK was observed. Samples with higher Rh content showed a power-law T-dependence, $\gamma \propto T^{\lambda-1}$ with $\lambda = 0.6$ and 0.67 for $x = 0.87$ and $x = 0.9$, respectively. For $x = 0.8$, the magnetic entropy increment ΔS is less than 0.4 $R\ln2$ up to 6 K. With increasing x this value becomes drastically reduced. An analysis of the entropy and the temperature dependence of the susceptibility at 2 K revealed some fraction of still unscreened magnetic moments, even at high x where the *average* T_K is already above 50 K. Thus, a broad distri-

bution of local T_K values with a tail down to $T_K \to 0$ is realized in this system [17].

The T-x phase diagram and the evolution of T_K in $CePd_{1-x}Rh_x$ raise questions concerning the mechanism behind the suppression of FM order and the presence of a QCP at the FM quantum phase transition. Below, we present results of thermal expansion, ac susceptibility and magnetization measurements in the region of the phase diagram where ferromagnetism disappears. The experiments were performed on poly- and single crystals that have been characterized before [16, 18].

The coefficient of volume thermal expansion, $\beta(T) = V^{-1}(dV/dT)$ (V: sample volume) is more singular than the specific heat $C(T)$ when approaching a pressure-sensitive QCP [19]. Consequently, the Grüneisen ratio $\Gamma \sim \beta/C$ must diverge algebraically in the approach of any HF QCP, as recently found for several KL systems exhibiting a QCP of AF nature [11]. Fig. 1a shows β of polycrystalline $CePd_{1-x}Rh_x$ with $0.8 \leq x \leq 0.95$ plotted as $\beta(T)/T$ vs. $\log T$. In agreement with $C(T)/T$ and $\chi_{ac}(T)$ results the minimum at $T \approx 0.25$ K in $\beta(T)/T$ marks the magnetic transition for $x = 0.8$. Upon increasing the Rh concentration, $\beta(T)/T$ shows no sign of phase transitions for $x = 0.87$ and 0.9, but rather diverges on cooling to 0.1 K. Note that for these concentrations $\beta(T)$ is negative and that for $x = 0.9$ the divergence is even larger than for $x = 0.87$, with absolute values comparable to those found in HF metals close to a QCP [11]. For the $x = 0.95$ sample, $\beta(T)/T$ is always positive, as expected for paramagnetic Ce systems, with smaller absolute values. These results are in contrast to those of specific-heat measurements on $0.8 \leq x \leq 0.95$ which clearly show a continuous decrease of the $C(T)/T$ values with increasing x, as expected when approaching the IV regime [17].

Analyzing the dimensionless Grüneisen ratio, defined as $\Gamma = V_m/\kappa_T \cdot \beta/C$, where V_m and κ_T denote the molar volume and isothermal compressibility, respectively, we find a striking deviation from the predicted stronger than logarithmic divergence for a QCP [19]: At $x = 0.87$, i.e., very close to the Rh-concentration for which the anomaly in $\chi_{ac}(T)$ disappears, an almost similar power-law behavior has been found for $C(T)/T$ and $\beta(T)/T$, leaving a virtually temperature independent Grüneisen ratio (see Fig. 1b). Thus, a QCP scenario can be discarded. Interestingly, in the paramagnetic regime, $x \geq 0.9$, $|\Gamma(T)|$ strongly increases on cooling in an almost logarithmic fashion and seems to saturate at the lowest temperatures. The negative Grüneisen ratio for $x = 0.87$ and 0.9 indicates an unusual volume dependence. For paramagnetic Ce systems, a positive Γ, as observed for $x = 0.95$, is expected, since the Kondo interaction, being the dominant energy scale, increases under hydrostatic pressure. On the other hand, a negative sign is usually associated with magnetic ordering due to the RKKY interaction, which decreases under hydrostatic pressure. Since $\Gamma < 0$ even in the paramagnetic regime, our data suggest the pres-
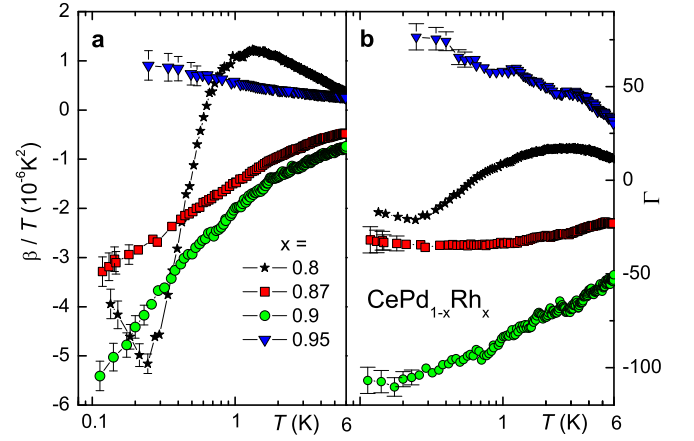

Figure 1: (color online) a: Volume thermal expansion $\beta(T)$ of $CePd_{1-x}Rh_x$ polycrystals plotted as β/T vs. $\log T$. b: Dimensionless Grüneisen ratio $\Gamma = V_m/\kappa_T \cdot \beta/C$ vs. $\log T$ with $V_m = 6.6 \cdot 10^{-5}$ m^{3}mol^{-1} and $\kappa_T = 1 \cdot 10^{-11}$ Pa^{-1}.

ence of substantial magnetic correlations in addition to the Kondo effect. In order to clarify the situation, we performed detailed magnetization and ac susceptibility measurements.

Low-temperature ac susceptibility was measured down to 20 mK at various frequencies ν on poly- and single crystals in the concentration range $0.6 \leq x \leq 0.9$. Although the absolute values of χ_{ac} decrease with increasing Rh content, it was possible to trace the transition temperature down to 25 mK for $x = 0.87$ (inset a of Fig. 2) [16]. The $x = 0.6$ sample clearly shows a FM phase transition at $T_C = 2.4$ K. The $x = 0.9$ sample does not show any ordering down to 20 mK. The pronounced χ_{ac} maxima of those samples with concentrations in between exhibit a frequency dependence. Poly- and single crystals show similar behavior. Single crystals were probed with the modulation field $\mu_0 h_{ac} \| c$. This transition appears to match several indications of spin-glass-type freezing. As displayed in Fig. 2, the $\chi_{ac}(T)$ signal of a single crystal with $x = 0.8$ shows a pronounced cusp in its real part χ' and a corresponding inflection point in the imaginary part χ''. Both signals display a clear frequency dependence at the temperature of the $\chi'(T)$ cusp, labeled T_C^* in order to distinguish it from the Curie temperature T_C found at lower Rh content. As in spin glasses $\chi'(T_C^*)$ is extreme sensitive to a superposed static magnetic field. In fact, only 15 mT are sufficient to depress the absolute value to $3/5$ of the signal in zero field. However, examining the relative temperature shift per decade in ν vs. x (inset b of Fig. 2), we find that this shift of about 3 to 10% per decade is considerably larger than in canonical metallic spin glasses which exhibit only 1 to 2%. The observed shift is similar in magnitude to the one observed in insulating spin glasses, but well below the value of about 28% observed in a superparamagnet [20].

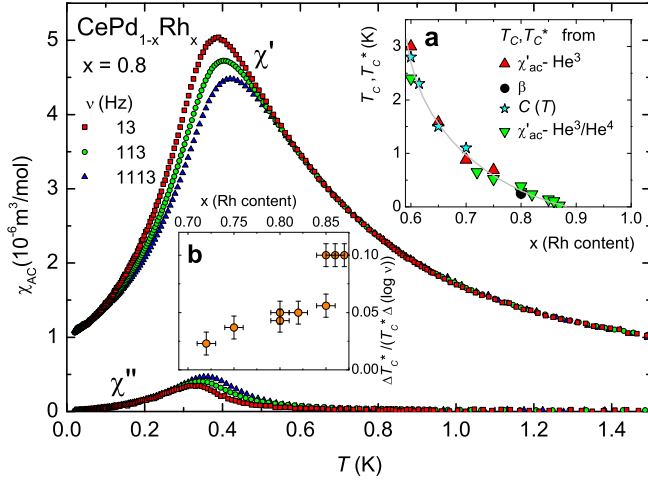The frequency dependence of $\chi_{ac}(T)$ provides evidence

Figure 2: (color online) Ac susceptibility of a single crystal ($x = 0.8$) for 3 selected frequencies in a modulation field of $\mu_0 h_{ac} = 11\,\mu$T. Inset a: Phase diagram of CePd$_{1-x}$Rh$_x$ for $x \geq 0.6$. Inset b: Relative temperature shift of the maximum in $\chi'(T)$ per frequency decade $\Delta T_C^*/(T_C^* \Delta(\log \nu))$ as a function of Rh content.

Figure 3: (color online) Dc magnetization M as a function of T in a constant field of 5 mT. FC (thick) and ZFC (thin) data on single crystals with Rh contents $0.6 \leq x \leq 0.92$ are shown down to 2 K. The onset of the temperature hysteresis, related to the formation of clusters (see text), is marked by the green arrow (exemplarily shown for $x = 0.65$). There is no cluster freezing for the sample with $x = 0.6$ above its T_C. Inset: low-T data for $x = 0.7$ measured at $\mu_0 H = 1$ mT.

for the existence of clusters in the system. The change of the magnitude of the shift suggests that the properties of the clusters, e.g., their size and/or coupling strength, vary with the Rh content. In fact, at $x \approx 0.85$ a rapid change of T_K was observed [16]. Very likely, the random distribution of Rh and Pd ligands creates regions with different local T_K values, due to differences in the hybridization of the Cerium $4f$ electrons with the valence electrons of these differing ligands. While Pd nearest neighbors tend to stabilize the Ce-moment, Rh ligands seem to screen it. The strength of the Kondo screening on a given Ce site thus depends sensitively on the local environment. This is in agreement with the analysis of $C(T)$ [17]. Since the Kondo interaction is rather extended across the lattice, this effect has to be interpreted in a different way than percolation effects caused by the dilution of magnetic moments. For $0.8 \leq x \leq 0.87$, the dimensionless Sommerfeld-Wilson ratio $R_W = \frac{\chi/\chi_0}{\gamma/\gamma_0}$ gives values between 20 and 30, leading to an estimated typical cluster size of about 5 spins [21]. To confirm the existence of freezing clusters, dc magnetization M was measured as a function of temperature on single crystals within the Rh concentration range $0.6 \leq x \leq 0.92$. The inset of Fig. 3 shows the results of field-cooled (FC) and zero-field-cooled (ZFC) measurements for $x = 0.7$ and $\mu_0 H = 1$ mT. Below the freezing temperature, a clear deviation is observed between FC and ZFC: While the FC curve saturates below T_C^*, the ZFC one exhibits a cusp at T_C^*. This demonstrates the irreversibility of the freezing process in agreement with our $\chi_{ac}(T)$ results. Remarkably, a small difference between the FC and ZFC curves exists also at much higher temperatures
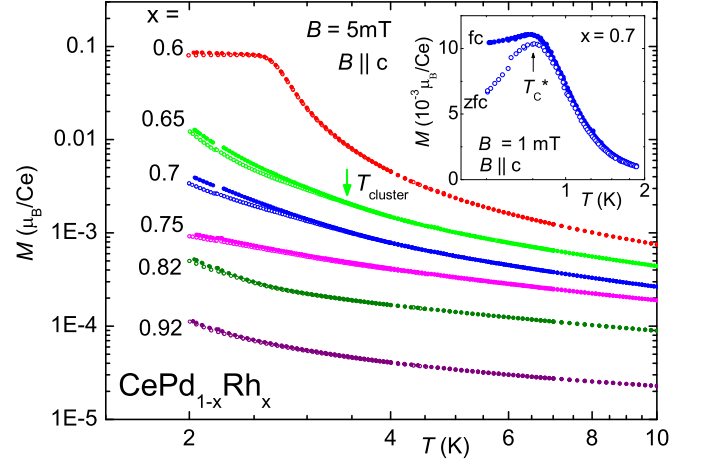
(cf. the main part of Fig. 3). We associate the temperature below which this irreversibility is observed with $T_{cluster}$, i.e., the characteristic temperature for the formation of short-range order in clusters. With increasing x, the low-T magnetization decreases by several orders of magnitude, indicative of a drastic reduction of the average moment per Ce-site and consistent with the strong reduction of the magnetic entropy [17].

The following scenario may account for all our findings: At temperatures high enough to overcome the Kondo screening, fluctuating magnetic moments exist on every Ce site; below the average Kondo temperature $\langle T_K \rangle$, an increasing number of f-moments becomes screened; however, due to the statistical distribution of Rh dopands on the Pd site and the strong dependence of the local T_K on the number of Pd nearest neighbors, there remain regions where the Kondo scale has not yet been reached; inside these regions, the f-moments are still unscreened; at even lower temperatures, $T < T_{cluster}$, these moments form clusters with predominantly FM coupling of the moments; within this temperature regime, the clusters are fluctuating independently; on further cooling below T_C^*, random freezing of the cluster moments sets in, leaving a static spin configuration. Such a scenario is compatible with all our observations: (i) The formation of clusters, (ii) their freezing, (iii) the small entropy at low temperatures and (iv) the negative sign of the thermal expansion, which points to short-range ordering even at temperatures much above T_C^*. As the broad distribution of local Kondo temperatures is responsible for the cluster formation, we propose to call the low-temperature state
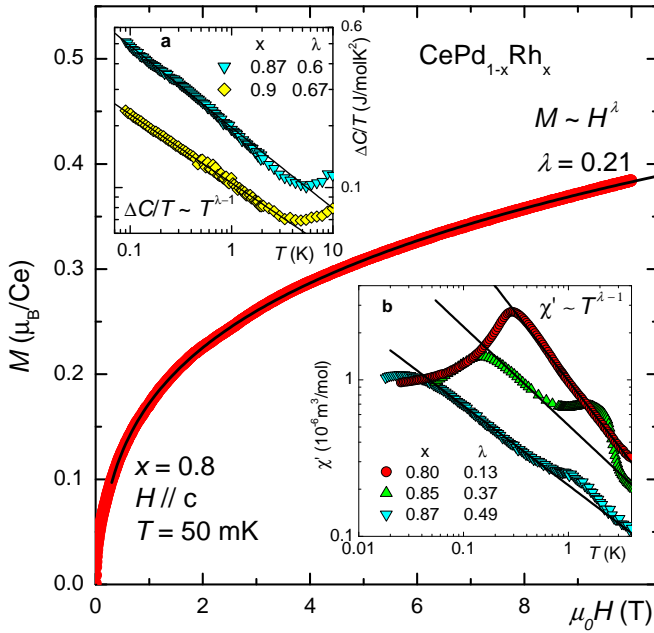
Figure 4: (color online) Field dependence of the magnetization M for a single crystal with $x = 0.8$ at 50 mK. The data follow a power-law function $M \propto H^{\lambda}$ (with $\lambda = 0.21$). Inset a: $4f$ contribution to the specific heat for polycrystals of $x = 0.87$ and $x = 0.9$ [17] as $\Delta C/T$ vs. T on double-log scale. Solid lines indicate power-law behavior. Inset b: ac susceptibility χ' of three polycrystals. The lines indicate fits with $\chi' \propto T^{\lambda-1}$ above T_C^*. The curves for sample $x = 0.85$ and 0.87 present two humps, which are due to impurity phases.

in $CePd_{1-x}Rh_x$ a "Kondo-cluster glass".

The decrease in concentration of the unscreened moments, along with the small cluster size, might explain why the freezing has been detected by $\chi_{ac}(T)$ down to very low T (for large x), but was not seen in other techniques, e.g., μSR or specific heat [22]. $CePd_{1-x}Rh_x$ is different from other Ce-systems like $CeCu_{1-x}Ni_x$ [23], where T_K is small in the entire composition range and the freezing could be observed by specific heat as well as by μSR experiments for all relevant concentrations.

Since the magnetic measurements reveal the existence of clusters, the observed NFL behavior may be described by the quantum Griffiths phase scenario [24, 25], which predicts $\chi' \propto C/T \propto T^{\lambda-1}$ and $M \propto H^{\lambda}$, with $0 \leq \lambda \leq 1$. As shown in Fig. 4, both the specific heat coefficient $\Delta C(T)/T$ and susceptibility $\chi'(T)$ follow a power-law behavior well above T_C^*, where the exponent varies systematically with x. Moreover, the field-dependent magnetization for a single crystal with $x = 0.8$ at 50 mK (below T_C^*) follows a power-law function with $\lambda = 0.21$, satisfactorily close to that found in $\chi'(T)$. A tiny hysteresis can be also observed with a coercive field of about 5 mT, but no step-like behavior can be resolved, in contrast to what has been seen in $CeCu_{1-x}Ni_x$ [23].

To conclude, the lack of a divergence of the Grüneisen ratio excludes a standard QCP in $CePd_{1-x}Rh_x$ and raises question about the origin of the pronounced NFL behavior. Whereas weak power-law divergences in the specific-heat coefficient may be considered as being due to a single-ion effect originating in the broad distribution of local Kondo temperatures [17], the observed negative sign of the thermal expansion strongly points to a co-operative effect. The detailed investigation of magnetic properties close to the disappearance of magnetic order reveals the formation of a "Kondo-cluster-glass" state, where the clusters result from regions of low local Kondo temperatures [26]. NFL effects in the specific heat, susceptibility and magnetization have been found to be compatible with the quantum Griffiths phase scenario.

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